HEALTH RISK ASSESSMENTS OF WASTE COMBUSTION EMISSIONS USING SURROGATE ANALYTE MODELS

THESIS

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THESIS

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Abstract

Open burn pits, at times a necessary method to control accumulating waste at military forward operating bases, have been implicated as the cause of respiratory disease and other illnesses. Exposure assessments of open burn pits are often complicated by a lack of sampling equipment and resources. This research investigated the hypothesis of carbon dioxide (CO_2) as a viable surrogate for particulate matter with diameter ≤ 2.5 μm ($PM_{2.5}$).

Large-scale solid waste combustion tests were monitored with real-time CO_2 and $PM_{2.5}$. Burn pile tests resulted in linear trends between mean $PM_{2.5}$ and mean CO_2 ($R^2 =$ 0.964 - 0.989). Comparing two burn box implementation methods, batch-feeding yielded $PM_{2.5}$ concentrations eight times lower than for a single loading of the burn box.

This pilot study demonstrates the feasibility of using CO_2 as a surrogate of $PM_{2.5}$ concentration as CO_2 sensors potentially provide a cost-effective solution for exposure monitoring in lieu of expensive particulate matter instruments. It also indicates the potentially beneficial reduction in particulate matter when using batch-feeding practices with burn boxes (versus open burning).

To my wife, who suffered with my talking about my thesis in my sleep (although I suspect

she found humor in this). Also to my son, off of whom I bounced ideas for this thesis.

Only 3 months old and he has contributed to the progress of science.

Acknowledgments

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HEALTH RISK ASSESSMENTS OF WASTE COMBUSTION EMISSIONS USING SURROGATE ANALYTE MODELS

I. Introduction

General Issue

Solid waste combustion is often employed at deployed locations to manage waste accumulation where other methods, such as landfills, are not available or practical. Incinerators and burn boxes may provide emission reductions, but not all installations have enough units, leaving open burning as a last resort option.

The current body of knowledge yields inconclusive evidence of association between exposure to open burn pits and increased risk of illnesses. An exhaustive study of exposure assessments from Joint Base Balad reviewed the known health effects associated with burn pit emission compounds, however could not definitively identify burn pit exposures as the causative factor for health effects (IOM, 2011). Several studies using data from an active epidemiological program, the Millennium Cohort Study, have analyzed certain exposures and reported illnesses. While some correlations were found, numerous confounding factors and biases hindered the identification of specific etiological exposures (Abraham et al., 2012; Powell et al., 2012; Rose et al., 2012; Smith et al., 2012). Further, the transient nature of deployed personnel results in numerous, different exposure profiles, complicating the determination of causation when symptoms appear during future medical evaluations. The uncertainties of the cause-effect relationship of waste combustion exposures coupled with various exposure profiles

requires adequate exposure assessments to reduce unknown factors in future studies and investigations.

Several challenges present themselves to the health risk assessor for exposure assessments of waste combustion emissions. Combustion emissions are mixtures of many chemical compounds, resulting from a complex of series and parallel chemical reactions with numerous outputs (Lobert and Warnatz, 1993). No single sampling and analysis method or direct reading instrument (DRI) can measure all possible compounds emitted. Additionally, equipment, supplies, reach-back support, and manpower are limited in a deployed setting.

Problem Statement

Department of Defense (DoD) health risk assessors often have limited sampling equipment and manpower to thoroughly assess exposures to solid waste combustion at deployed installations. It is hypothesized that an analyte which can be easily monitored, such as carbon dioxide (CO_2), can be used as a surrogate to estimate exposures to pollutants which would require expensive or specialized equipment. However, current technology and procedures complicate the use of exposure assessments conducted using models, requiring additional considerations to facilitate exposure assessments in lieu of expensive monitoring equipment.

Research Questions

The objective of this research is to develop an improved protocol for DoD health risk assessors for the exposure assessment of waste combustion products in a deployed environment. A review of the body of knowledge and recent AFIT research efforts will

identify the pollutants of concern (POCs). Data analysis from a large-scale sampling project of municipal waste open burning will be conducted to determine if a surrogate analyte can be used to estimate the exposure to POCs. This research will answer the following questions:

1. Can surrogate analytes be used to estimate exposures to other POCs which may be too resource-intensive to otherwise sample on a routine basis?

   1.1. What POCs can be estimated using a surrogate analyte?

2. What is a potential assessment strategy for a risk assessor to estimate exposures throughout the installation?

Scope and Approach

This research was conducted using real-time CO_2 and particulate matter with diameter ≤ 2.5 µm ($PM_{2.5}$) data collected from a large-scale solid waste combustion tests conducted at Tooele Army Depot (TEAD), Utah. CO_2 was selected as a potential surrogate analyte as real-time monitors are relatively inexpensive and readily available to health risk assessors at deployed locations. Additionally, several CO_2 levels were established as "triggers" to initiate and terminate other sampling trains via computer programs in order to preserve battery charge of other sample trains; carbon monoxide (CO) monitors were not selected for this operation due to anticipated errors related with response-time performance. $PM_{2.5}$ was selected as the POC due to increasing implications of adverse health effects. Analytical methods include analysis of variance (ANOVA), Tukey's test, and linear regression. An overview of exposure assessment procedures addresses potential application of a surrogate model for burn pit exposures and identifies potential challenges for consideration.

Significance

       This thesis continues research conducted by three AFIT alumni based upon burn pit exposures (Oppenheimer, 2012; Rinker, 2011; Woodall, 2012). The focus of this thesis is to test the hypothesis that a surrogate analyte can estimate exposures to pollutants of concern, thus providing a viable tool to a health risk assessor where conventional methods are not available. Further, the analysis conducted in this research may be applicable to future studies or implementation in environmental health risk assessments for communities with similar exposures.

Preview

       This thesis was written in the scholarly article format. The article was written with the intent for submission to *Environmental Health Perspectives* journal. This article is presented as Chapter II of this thesis, reformatted to maintain consistency within this document. The article primarily addresses the surrogate analyte hypothesis (Thesis Questions 1 and 1.1) as it may be appropriate for the general community in addition to military applications. Chapter III concludes the thesis, addressing all thesis questions and their implications. Appendices provide expanded material, such as an expanded literature review and discussion of thesis questions not addressed in the article.

II. Scholarly Article

Written for consideration of submission to *Environmental Health Perspectives* journal
(http://ehp.niehs.nih.gov/)

HEALTH RISK ASSESSMENTS OF WASTE COMBUSTION EMISSIONS USING

SURROGATE ANALYTE MODELS

Michael A. Schmidt, Dirk P. Yamamoto, Darrin K. Ott, LeeAnn Racz, and Daniel
Schneider

Abstract

Background.

Open burn pits, at times a necessary method to control accumulating waste at
military forward operating bases, have been implicated as the cause of respiratory disease
and other illnesses. Exposure assessments of burn pit emissions are often complicated
by a lack of sampling equipment, laboratory support, or direct reading instruments.

Objectives.

This pilot study investigated whether carbon dioxide (CO_2) is a viable surrogate
analyte for particulate matter with diameter ≤ 2.5 µm ($PM_{2.5}$), enabling risk assessments
without strict dependence on traditional air sampling equipment or expensive direct
reading instruments. Differences between burn pile and burn box emissions were also
evaluated.

Methods.

Municipal and military depot solid waste was combusted in burn piles and burn boxes, in which 1-second CO_2 and $PM_{2.5}$ measurements were recorded. Data were analyzed using analysis of variance, Tukey's tests, and linear regression techniques.

Results.

Four burn pile tests demonstrated a linear trend between mean CO_2 and $PM_{2.5}$ ($R^2 = 0.964 - 0.989$). For tests using equivalent waste sources, $PM_{2.5}$ emissions for all burn box tests were statistically different than burn pile emissions. Batch-feeding yielded $PM_{2.5}$ concentrations eight times lower than for a single loading of the burn box.

Conclusions.

This pilot study indicates the potentially beneficial reduction in particulate matter when using batch-feeding practices with burn boxes (versus open burning). It also demonstrates the feasibility of using CO_2 as a surrogate of $PM_{2.5}$ concentration. CO_2 sensors potentially provide a cost-effective solution for exposure monitoring in lieu of expensive particulate matter instruments. Applications of the proposed model may extend beyond military use, such as risk assessments for communities near industries or other combustion-related exposure assessments.

Introduction

Waste management is necessary and important at United States (US) military forward operating bases (FOBs) for volume reduction and vector control purposes. Transportation of solid waste to other sites, such as host country landfills, may not be a viable option. The expedient method often relied upon is combustion. Well-established

FOBs may be equipped with incinerators or burn boxes that are designed to control emissions. Burn boxes, also referred to as air curtain burners or air curtain destructors, typically use blowers to form a curtain of air above the fire in order to recirculate emissions, theoretically improving combustion. Incinerators are often designed to subject emissions to a secondary combustion reaction. Open burning is intended to be a last resort option, in the absence of burn boxes, incinerators, or other means of waste management.

Combustion emissions are complex and present numerous technical challenges to a health risk assessor. Under ideal conditions, combustion results in the generation of carbon dioxide (CO_2) and water. Incomplete combustion results from several non-ideal factors such as high density of combustible material, high moisture content, and poor oxygen (O_2) flow, which are inherent with large piles of solid waste. The classes of compounds emitted from open burning of solid wastes are numerous and include: carbon monoxide (CO), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), particulate matter (PM), volatile organic compounds (VOCs), and metals. These mechanisms, burn parameters, pollutants, and their relationships to waste combustion have been researched extensively (Gullett and Raghunathan, 1997; EPA, 1997; Gullett et al., 2001; Lemieux et al., 2000). Efforts have been made to quantify emission factors of these pollutants and observe how combustion parameters affect combustion efficiency for military waste combustion (Aurell et al., 2012; Woodall et al., 2012) and residential backyard burn barrels (EPA, 2002; Gullett et al., 2001), which have been identified as a significant source of pollutants in rural communities.

Various burn stages occur over the course of combustion, favoring complete or incomplete combustion mechanisms. For the purposes of this research, the burn stages are simplified as either "flaming" or "smoldering". The flaming stage is characterized by temperatures as high as 2200 K (1927 °C), resulting in visible flames and increased oxidation rate of CO into CO_2 in addition to the formation of soot. Conversely, the smoldering stage has a lack of visible flames, lower CO_2 emissions, and increasing PM size due to lower combustion temperatures (Lobert and Warnatz, 1993).

Concerns among the public and military personnel have been raised after burn pits were suspected as the cause of reported health effects, including Gulf War Syndrome, asthma, constrictive bronchiolitis, and obstructive pulmonary disease (Abraham et al., 2012; Rose et al., 2012). Among burn pit emissions, PM with diameter ≤ 2.5 µm ($PM_{2.5}$) has been correlated with various health effects, such as myocardial infarctions, pulmonary inflammation, and cancer (Polichetti et al., 2009; Pope et al., 2002). An exhaustive study between burn pit exposures and long-term health effects was unable to conclude burn pit exposures as etiological factors (IOM, 2011). Several studies using data from an active epidemiological program, the Millennium Cohort Study, have analyzed certain exposures and reported illnesses. While some correlations were found, numerous confounding factors and biases hindered the identification of specific etiological exposures (Abraham et al., 2012; Powell et al., 2012; Rose et al., 2012; Smith et al., 2012). Further, the transient nature of deployed personnel results in numerous, different exposure profiles, complicating the determination of causation when symptoms appear during future medical evaluations. The uncertainties of the cause-effect relationship of waste combustion exposures coupled with various exposure profiles

requires adequate exposure assessments to reduce unknown factors in future studies and investigations.

Several studies exist which use surrogate analytes to estimate exposures of other pollutants. One study evaluated wild land firefighters' exposures during controlled burns (Reinhardt and Ottmar, 2004). The authors observed linear relationships ($R^2 = 0.62 -$ 0.86) between the time-weighted average of several combustion products, such as CO, benzene, formaldehyde, and PM with diameter ≤ 3.5 µm. These relationships can then be used to estimate exposures where data gaps existed. Olorunfemi et al. observed a similar trend between CO and $PM_{2.5}$, suggesting pollutants emitted from vegetation combustion are linearly related (Olorunfemi et al., 2011).

This research examined if such trends extend to solid waste combustion and if surrogate models are possible assessment tools where resources are limited. The study was limited to CO_2 and $PM_{2.5}$, which were measured in real-time at multiple locations. CO_2 was selected as the surrogate compound as it is easily measured by direct reading instruments (DRIs); CO may be another potential surrogate analyte (Reinhardt and Ottmar, 2004), but was not adequately measured for the analysis in this study. $PM_{2.5}$ was selected as the pollutant for surrogate analysis due to increasing implications of adverse health effects (Polichetti et al., 2009; Pope et al., 2002) as well as the often prohibitive cost of particulate matter DRIs, which typically cost more than CO_2 DRIs.

Methodology

    Air Sampling.

    This study consisted of six large-scale solid waste combustion tests, consisting of four open burn piles and two burn box tests, conducted at Tooele Army Depot (TEAD), Utah. The burn piles, approximately 6,500 kg for each test, were windrow-shaped with dimensions approximately 25 m × 2.5 m × 1 m, configured with the length in the direction of forecasted winds (Figure 1A). The burn box used in this study was a McPherson model M10E (Figure 1C). Municipal waste from the local community was used for all burns, with the exception of one open burn pile test which used TEAD-generated waste. Except for minor compositional differences, the waste used in this project was representative of waste characterized at FOBs (Aurell et al., 2012; Oppenheimer, 2012). Waste composition for the experiment is summarized in Supplemental Material, Table 3.

Figure 1: Burn pile test with (A) crane and (B) aerostat; (C) burn box test.

Transition from flaming to smoldering stages was visually determined after a noticeable decrease in flames and increase in smoke, which typically occurred within one hour from ignition. Smoldering stages lasted approximately 1-2 hours, at which time the fire was extinguished for safety purposes and data collection was halted. Measurements were recorded during the burn tests and therefore did not include recordings before ignition or after the fires were extinguished. Additionally, sampling was temporarily halted to facilitate cartridge change out for other sample media. One burn box test, Burn Box 1, was conducted by adding 16 waste feeds, each approximately 290 kg, throughout the test, effectively maintaining a flaming stage. Burn Box 1 data collection was conducted in four segmented sampling times, facilitating cartridge change out. In

contrast, Burn Box 2 was executed with a single charge of waste with no additions through the test duration. Table 1 summarizes the burn test and sampling durations.

Table 1: Burn test matrix.

Burn Number	Burn Duration (hh:mm)	Sample Collection Time[a] (h:mm:ss)
Burn Pile 1	2:53	2:09:58
Burn Pile 2	2:46	2:03:44
Burn Pile 3	2:05	1:14:11
Burn Pile 4	2:05	1:31:25
Burn Box 1[b]	8:10	1:06:10
		2:57:41
		1:52:07
		1:31:35
Burn Box 2	2:07	1:15:05

[a] With respect to the crane sample.
[b] Sample collection times for four sub-test samples.

Two air sampling apparatuses, called Flyers, were assembled with multiple sampling trains for CO_2, $PM_{2.5}$, VOCs, PCDDs, PCDFs, PAHs, and PCBs, of which were the subject of a parallel study with a focus on emission factors (Aurell et al., 2012). CO_2 levels were pre-programmed as "triggers" to initiate and terminate other sampling trains (to preserve battery charge) for the analysis of emissions factors from flaming and smoldering stages in the study conducted by Aurell et al (2012). CO monitors were not selected for this operation due to anticipated errors related with response-time performance. One of the Flyer assemblies is presented in Figure 2. Real-time CO_2 and $PM_{2.5}$ were measured with a LI-820 CO_2 Analyzer (LI-COR®, Lincoln, Nebraska) and DustTrak™ 8520 (TSI Inc., Shoreview, Minnesota), respectively, and measurements were recorded at 1-second intervals. One of the Flyers was placed on a crane, which

sampled the base of the emission plume (Figure 1A). The other Flyer was attached to an

aerostat (weather balloon), which was positioned within the plume downwind,

approximately 10 m in elevation (Figure 1B).
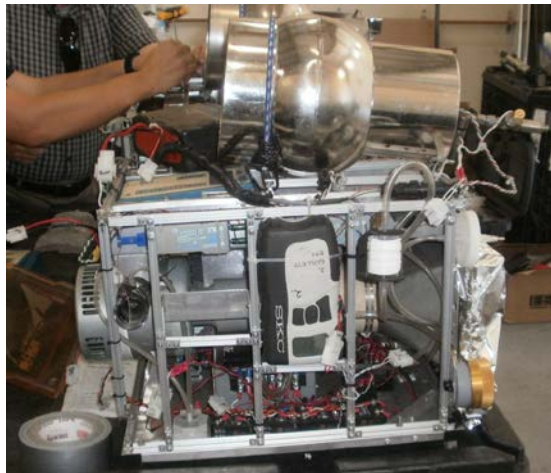
Figure 2: Flyer apparatus for crane and aerostat sampling platforms.

In addition to the Flyers, three ground stations were positioned approximately

40 m, 60 m, and 80 m downwind of the burn pile in the direction of the forecasted

predominant winds. The ground stations were equipped to measure real-time CO_2 and

$PM_{2.5}$. Aerostat data was not available for Burn Pile 2 and both burn box tests only

included crane sampling platforms.

Data Analysis.

Real-time measurements of CO_2 and $PM_{2.5}$ fluctuated significantly from a

second-to-second basis; therefore, plots were constructed using 5-minute averages to

illustrate the overall emission trends. The time scale was adjusted to percent of duration

to permit comparisons between burn tests. As discussed earlier, CO_2 concentrations were

expected to decrease as time progressed. PM is emitted during both flaming and smoldering stages, with size distributions shifting towards higher occurrence of larger PM sizes during smoldering. $PM_{2.5}$ concentration was anticipated to increase over the duration of combustion; analysis of particle size distributions was beyond the scope of this study.

Analysis of variance (ANOVA) and Tukey's tests were performed for CO_2 and $PM_{2.5}$ crane samples, using $JMP^®$ 9.0 (SAS Institute, Inc., Cary, NC), to determine if there was a statistical difference between the burn methods. For Burn Box 1, samples corresponding to each cartridge change out were further analyzed to determine if any significant differences of CO_2 and $PM_{2.5}$ emissions were attributable with the loading in batches compared to a single charge of waste. The selected α for p-value comparison was 0.05, below which burn tests were statistically different.

Finally, the trend between mean CO_2 and mean $PM_{2.5}$ among each sampling platform (crane, aerostat, and ground stations) was analyzed for each burn pile test using Microsoft Excel 2010$^®$ to perform linear regression. Burn box tests were excluded from this analysis as the crane was the only sampling platform used.

Results

The histograms for CO_2 and $PM_{2.5}$ emissions measured at the base of the plume appeared to be log-normally distributed, but displayed a significant right-skewed pattern. Burn Pile 1 crane data histograms are shown in Figures 3 and 4; comparable distribution patterns were observed for the other burn tests.

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The farthest ground stations (80 m from the burn pile) resulted in similarly right-skewed distributions, with highest frequencies near ambient measurements. Histograms for 80 m ground stations from Burn Pile 1 are shown in Figures 5 and 6.
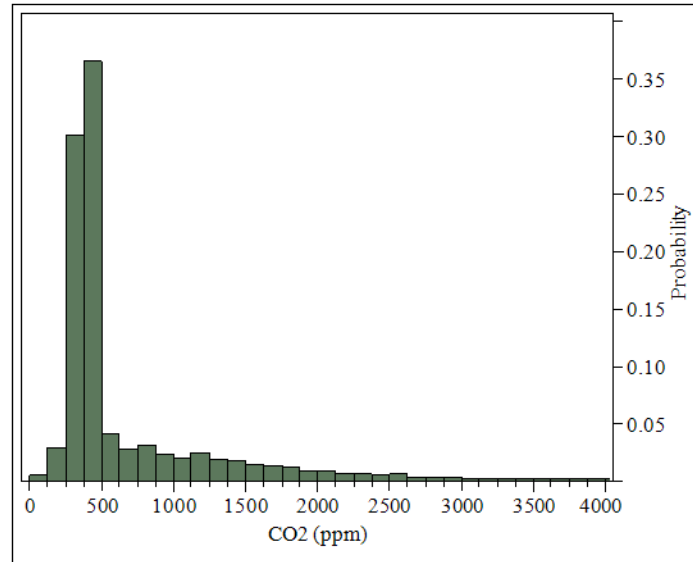
Figure 3: CO_2 distribution at the plume base for Burn Pile 1. Tail truncated at 4,000 ppm to illustrate distribution curve shape (maximum CO_2 = 8,826 ppm).
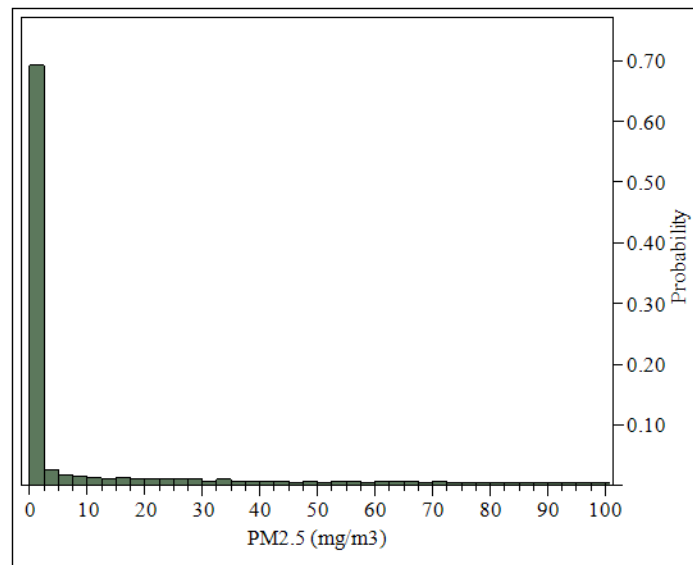
Figure 4: $PM_{2.5}$ distribution at the plume base for Burn Pile 1. Tail truncated at 100 mg/m^3 to illustrate distribution curve shape (maximum $PM_{2.5}$ = 209 mg/m^3).

Figure 5: CO_2 distribution 80 m ground-level from Burn Pile 1. Tail truncated at 465 ppm to illustrate distribution curve shape (maximum CO_2 = 544 ppm).
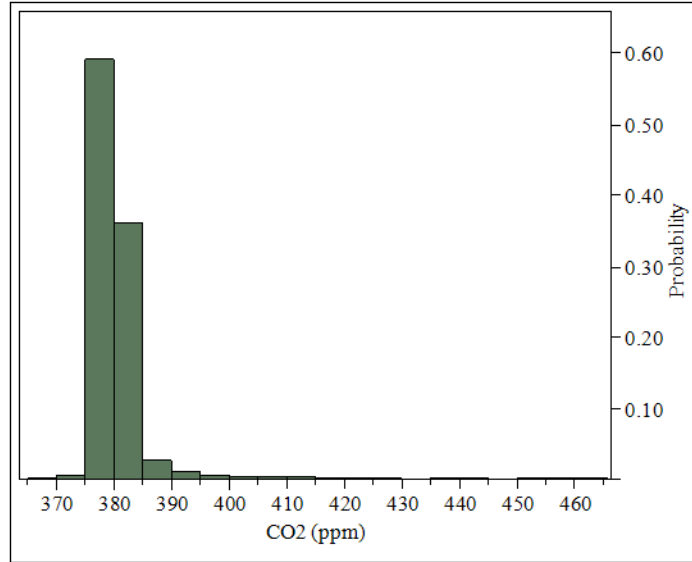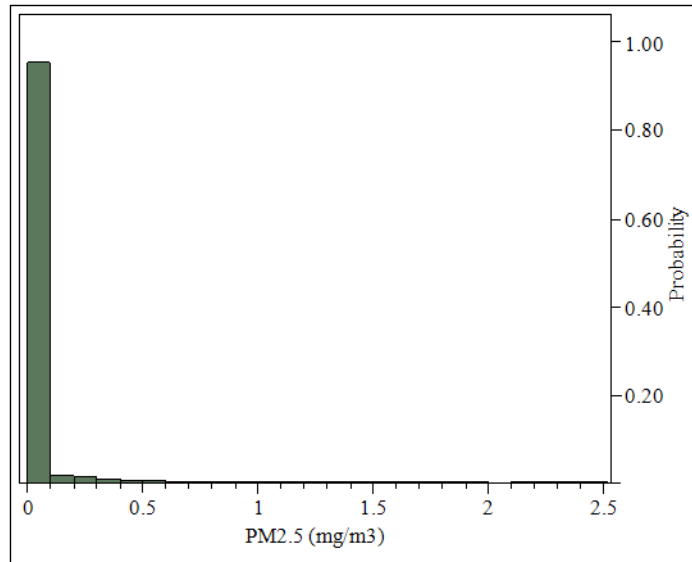

Figure 6: $PM_{2.5}$ distribution 80 m ground-level from Burn Pile 1. Tail truncated at 2.5 mg/m^3 to illustrate distribution curve shape (maximum $PM_{2.5}$ = 14.0 mg/m^3).

Burn Pile and Burn Box Emission Analysis.

All crane samples, with the exception of Burn Pile 1, were initiated after ignition (25 – 60 minutes); for these tests, emission concentrations during the flaming stage were undetermined. Five-minute average CO_2 and $PM_{2.5}$ concentration plots are shown in Figures 7 and 8 for Burn Piles 1 and 4, respectively. The Burn Pile 4 plot shows the general trends expected from the static fire model described by Lobert and Warnatz (1993). CO_2 increased and peaked at 45% of the burn duration, presumably coinciding with the flaming stage, and then decreased as the test continued into the smoldering stage. $PM_{2.5}$ increased and peaked at 45% of the burn duration, with a slight decrease as smoldering progressed. For Burn Pile 1, CO_2 fluctuated between approximately 400 and 1,100 ppm throughout the test. $PM_{2.5}$ generally increased and peaked at approximately 80% of the burn time and then decreased. The plots of the other burn tests demonstrated similar peaking tendencies, but with variations in observed trends.
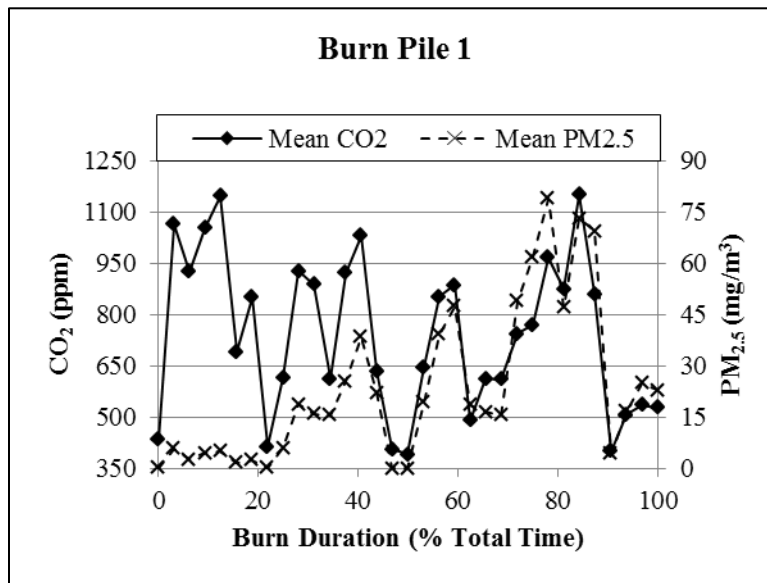
Figure 7: 5-minute average concentration plotted versus time (Burn Pile 1).
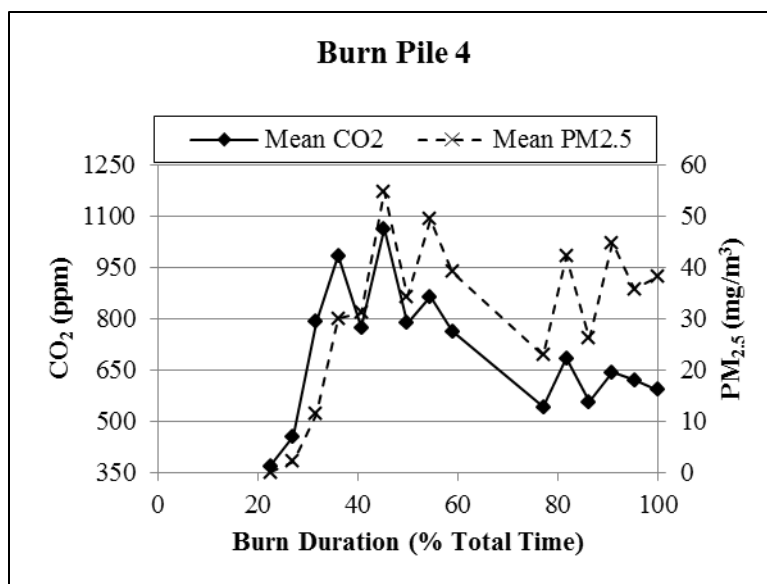
Figure 8: 5-minute average concentration plotted versus time (Burn Pile 4).

ANOVA and Tukey's tests were used to compare the mean CO_2 and $PM_{2.5}$ for all pairs of burn tests. Among the burn pile tests, only Burn Piles 1 and 4 had mean CO_2 concentrations which were not statistically different (p-value 0.990); all other burn pile comparisons for mean CO_2 and $PM_{2.5}$ were statistically different (all p-values < 0.0001). Among the burn box tests, Burn Box 1 and Burn Box 2 resulted in mean CO_2 concentrations not found to be statistically different (p-value 0.978), but had statistically different mean $PM_{2.5}$ concentrations (p-value < 0.0001). The mean $PM_{2.5}$ concentration for Burn Box 2 was approximately eight times that of Burn Box 1 (44.4 mg/m^3 compared to 5.55 mg/m^3). Comparing burn pile and burn box tests, Burn Pile 3 was not statistically different from Burn Box 1 or Burn Box 2 for mean CO_2 concentrations (p-values 0.793 and 0.998, respectively), nor were Burn Pile 3 and Burn Box 1 observed as statistically different for mean $PM_{2.5}$ concentrations (p-value 0.332). All other burn test comparisons were found to be statistically different with p-values < 0.0001. See Supplemental

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Material, Table 4, for a summary of Tukey's test results for burn test pair concentrations which were not statistically different.

Surrogate Model Analysis.

Mean $PM_{2.5}$ and CO_2 pairs from each sample location for all burn pile tests resulted in a linear regression with $R^2 = 0.259$ (Figure 9).
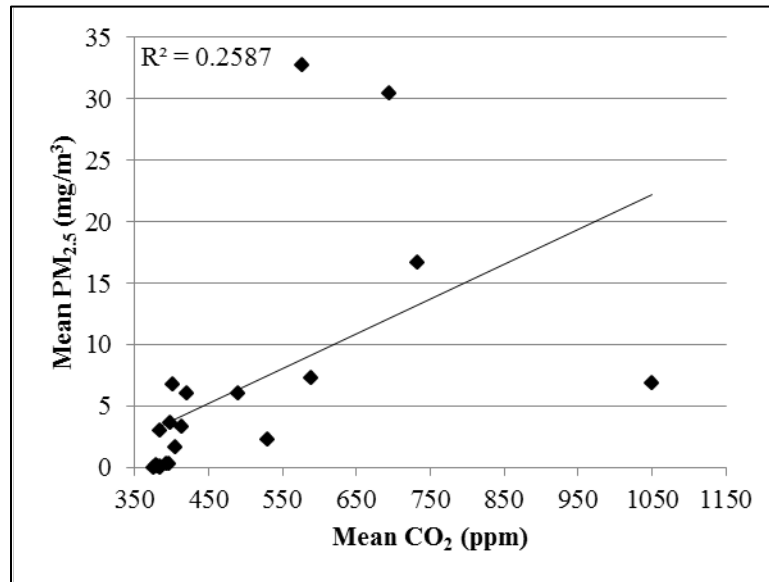
Figure 9: Linear regression of all burn pile test measurements.

Further analysis included linear regression for each burn pile test (Supplemental Material, Figures 14 - 17). The background values for mean CO_2 (375 ppm) and $PM_{2.5}$ (0.0038 mg/m^3) were included as a data point for each burn test. Linear regression for burn pile tests, when considering each burn test as an independent analysis, resulted in $R^2 = 0.964 – 0.989$. CO_2 and $PM_{2.5}$ concentrations for the TEAD experiment are summarized in Table 2.

Table 2: Summary of TEAD experiment measurements.

Burn Number	Waste Type	Sampling Platform	Mean ± SD CO$_2$ (ppm)	Mean ± SD PM$_{2.5}$ (mg/m^3)
Background	N/A	N/A	375[a]	0.004[a]
Burn Pile 1	Municipal	Crane	732 ± 885	16.696 ± 39.696
		Aerostat	589 ± 366	7.288 ± 12.690
		Ground (40 m)	396 ± 28	0.288 ±1.711
		Ground (60 m)	385 ± 12	0.087 ± 0.541
		Ground (80 m)	381 ± 6	0.039 ± 0.254
Burn Pile 2	Municipal	Crane	577 ± 423	32.712 ± 55.440
		Ground (40 m)	421 ± 89	5.998 ± 11.404
		Ground (60 m)	402 ± 33	6.796 ± 11.481
		Ground (80 m)	384 ± 20	2.979 ± 5.256
Burn Pile 3	Depot	Crane	1,049 ± 1,082	6.815 ± 11.964
		Aerostat	529 ± 266	2.259 ± 3.318
		Ground (40 m)	393 ± 62	0.260 ± 0.772
		Ground (60 m)	380 ± 24	0.174 ± 0.530
		Ground (80 m)	384 ± 7	0.019 ± 0.078
Burn Pile 4	Municipal	Crane	695 ± 790	30.458 ± 56.230
		Aerostat	398 ± 91	3.653 ±12.843
		Ground (40 m)	491 ± 246	6.047 ± 12.634
		Ground (60 m)	414 ± 81	3.299 ± 8.184
		Ground (80 m)	404 ± 53	1.675 ± 4.256
Burn Box 1	Municipal	Crane	1,071 ± 1,154	5.549 ± 15.691
Burn Box 2	Municipal	Crane	1,062 ± 736	44.369 ± 39.178

[a]Standard deviations for background values were not available.

Discussion

Burn Pile and Burn Box Emission Analysis.

Although some burn tests resulted in temporal CO_2 and $PM_{2.5}$ plots with the expected trends (described earlier), other burn tests showed no such discernible patterns. The reason for this is presumably attributable to the complex factors affecting burn characteristics typical of dynamic fires (Lobert and Warnatz, 1993). Burn Box 1 resulted in higher CO_2 peaks and lower $PM_{2.5}$ peaks than Burn Box 2. This is consistent with the hypothesis that maintaining a flaming stage yields higher combustion efficiency, indicative of higher CO_2 emissions and lower pollutants (e.g. $PM_{2.5}$), as demonstrated by Aurell et al (2012).

Tukey's tests showed the burn piles were all statistically different for $PM_{2.5}$ emission concentrations. Burn Box 1 resulted in lower $PM_{2.5}$ concentrations than all other burn tests. Multiple additions of waste may have increased combustion efficiency, leading to lower emissions of pollutants, compared to the burn piles which were visibly observed to transition to smoldering stages. Burn Box 2, implementing the single-charge method, resulted in higher $PM_{2.5}$ concentrations than all other burn tests. It is noted that the number of tests was limited and further research is warranted.

Surrogate Model Analysis.

$PM_{2.5}$ and CO_2 linear fit plots for four burn pile tests yielded $R^2 = 0.964 – 0.989$, suggesting that CO_2 is a valid surrogate analyte for estimating $PM_{2.5}$ exposures. Each regression resulted in different equations, yet the general trend may be simply defined by the background and crane CO_2 and $PM_{2.5}$ measurements, with interpolation methods for CO_2 at a location of interest.

Other studies have shown similar results for vegetative fires (Olorunfemi et al., 2011; Reinhardt and Ottmar, 2004), but differ in that multiple exposure incidents spanning a course years were compiled into a single regression analysis. One assumption necessary for those studies is that each wildfire event resulted in emission profiles comparable to each other. This study, however, resulted in different $PM_{2.5}$ concentrations for each burn test, implying such an assumption cannot be made for solid waste combustion. Thus, the surrogate model presented in this research suggests that measurement of both analytes at the plume source and background is necessary in order to estimate concentrations.

Regression analysis was based on a small set of data points; each burn test resulted in six data points, including the background data, for each regression (except Burn Pile 2 due to a lack of aerostat data). Similar studies of wildfire exposures included numerous measurements over wide concentration ranges, resulting in linear trends (Olorunfemi et al., 2011; Reinhardt and Ottmar, 2004). Additional research, including more sampling locations that canvass multiple directions and distances with respect to the burn site, may be warranted.

Limitations.

The histograms for CO_2 and $PM_{2.5}$ (Figures 3 – 6) and the standard deviations, relative to the respective mean values (Table 2), suggest high variance and show that the emission distributions were not log-normal. Additionally, the response time and sensitivity of the monitors were possible sources of error. The surrogate model analysis included all 1-second measurements over the entire burn duration observed; the sample means analyzed were assumed to be approximately equivalent to the population mean as a result of the large number of measurements associated with each data point.

CO_2 variations during the experiment were assumed to be attributable to the burn tests, as the site was relatively remote and not subject to other significant sources of CO_2. However, practical applications of a surrogate model may include locations where CO_2 fluctuations due to other sources, such as human exhalation, may adversely affect model results. CO may be another surrogate, with fewer sources confounding levels attributable to solid waste combustion operations, warranting future research.

As the experiment was in a remote location, this model may be valid for CO_2 and $PM_{2.5}$ exposures at regions under the influence of waste combustion sources only. Other significant sources, such as generator or vehicle exhaust, may confound the results.

Conclusions

The use of CO_2 as a surrogate analyte to model $PM_{2.5}$ exposures was found to be a feasible tool. CO_2 sensors may provide a cost-effective solution for exposure monitoring in lieu of air sampling methods, requiring special collection kits and laboratory analysis, or dependence on expensive DRIs to measure particulate matter. Should a surrogate model be validated and implemented, health risks assessments for solid waste combustion would be available where otherwise no exposure estimate would be possible. This model requires background and emission measurements of each analyte for the specific waste combustion activity for valid exposure estimates. Further research specific to solid waste combustion may show exposures to other pollutants can be estimated with an acceptable level of accuracy. Other future research efforts should consider a greater spatial array of sampling locations.

Although the motivation for this research was burn pit exposures at FOBs, the potential use of such surrogate modeling may be useful for risk assessments in other settings. For example, many cities readily conduct air quality measurements, to include PM data. Environmental health risk assessors may leverage this data in conjunction with plume monitoring at a source of interest, such as a local landfill incinerators. Another use may include risk assessments for rural communities in which burn barrels are commonly used by residents.

Supplemental Material

Table 3: TEAD experiment waste composition (adapted from Oppenheimer, 2012).

Waste component	TEAD Municipal Waste	TEAD Depot Waste
Plastics		
PETE	2.23 %	3.70 %
HDPE	2.03 %	1.23 %
LDPE	4.05 %	4.17 %
PP	1.32 %	0.62 %
PVC	0.00 %	0.00 %
PS	1.22 %	0.46 %
Polycarbonate	1.22 %	0.00 %
Unidentified Appliances	2.63 %	0.00 %
Foam	0.00 %	1.08 %
Misc.	5.88 %	1.08 %
Total	**19.5** %	**12.3** %
Wood	**10.0 %**	**12.0 %**
Metals		
Aluminum/Tin	3.44 %	0.46 %
Iron/Steel	3.04 %	11.11 %
Copper	0.00 %	1.39 %
Total	**6.5** %	**13.0** %
Glass	**0.4 %**	**1.1 %**
Misc. Combustibles		
Paper	36.88 %[a]	16.98 %
Cardboard		31.33 %
Clothes and Fabrics	3.85 %	0.31 %
Vegetation	5.67 %	7.41 %
Food Waste & Diapers	15.81 %	4.32 %
Total	**62.2** %	**60.4** %

[a] Paper and cardboard were reported as one item.

Figure 10: 5-minute average concentrations plotted versus time (Burn Pile 2). Spikes in PM2.5 at the far right are most likely due to smoke from quenching of the fire prior to halting data collection.
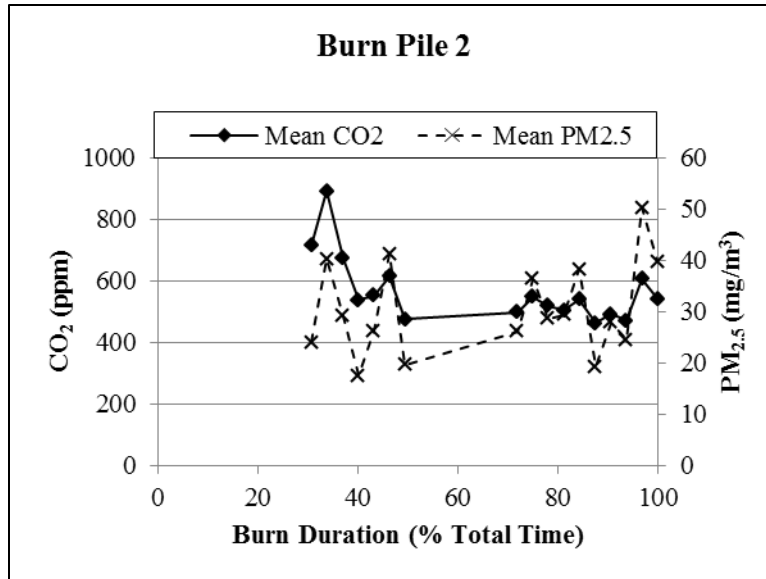

Figure 11: 5-minute average concentrations plotted versus time (Burn Pile 3). Spikes in PM2.5 at the far right are most likely due to smoke from quenching of the fire prior to halting data collection.
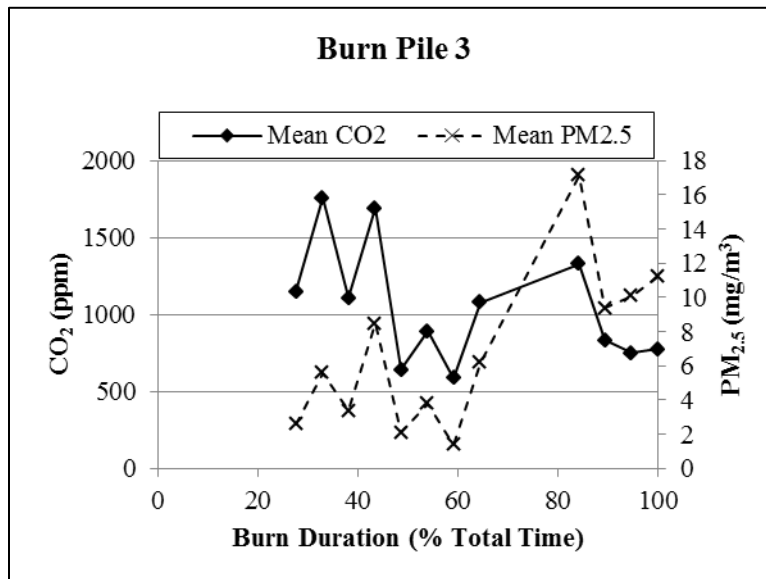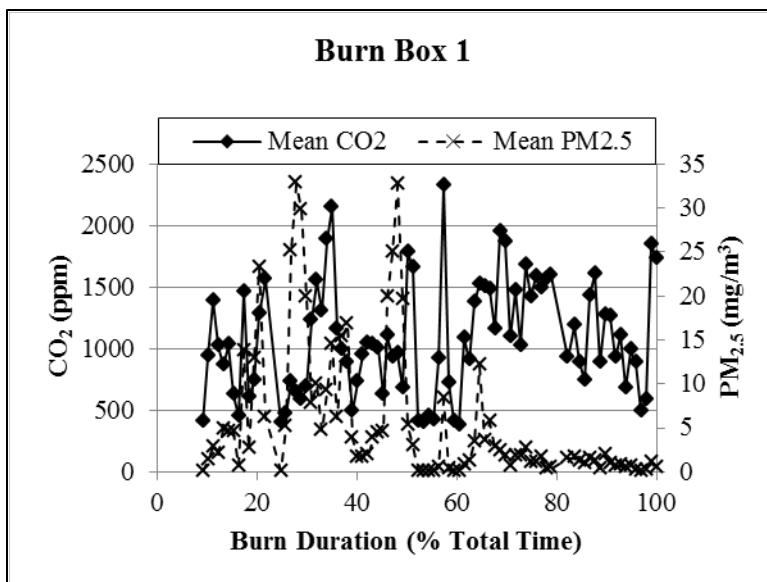
Figure 12: 5-minute average concentrations plotted versus time (Burn Box 1).
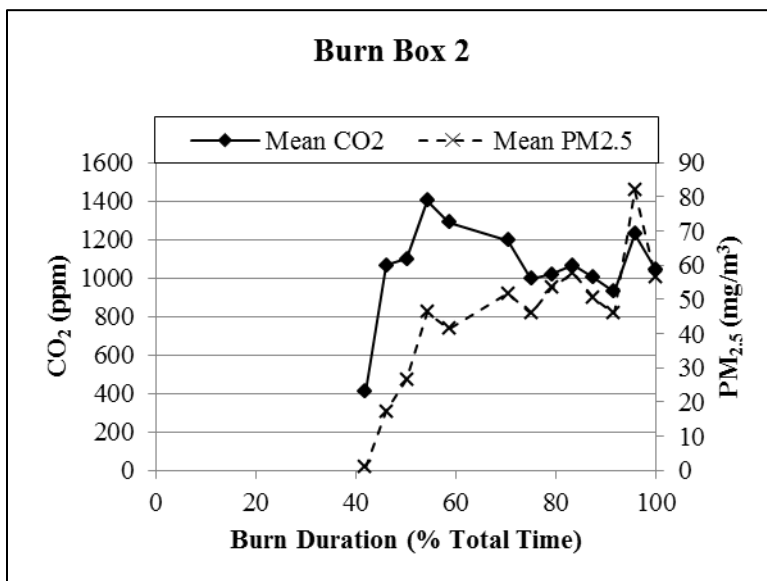
Figure 13: 5-minute average concentrations plotted versus time (Burn Box 2).

Table 4: Summary of Tukey's test results for pairs not statistically different.

Burn Box 1 Assumption	Analyte (Means)	Burn Test Comparison Pair	p-Value
One Test	CO_2	BP3 - BB1	0.7933
		BB1 - BB2	0.9780
		BP1 - BP4	0.9902
		BP3 - BB2	0.9976
	$PM_{2.5}$	BP3 - BB1	0.3318
Four Sub-Tests	CO_2	BP3 - BB1D	0.9995
		BP1 - BP4	0.9995
		BP3 - BB2	0.9999
		BB1D - BB2	1.0000
	$PM_{2.5}$	BP3 - BB1A	0.9897
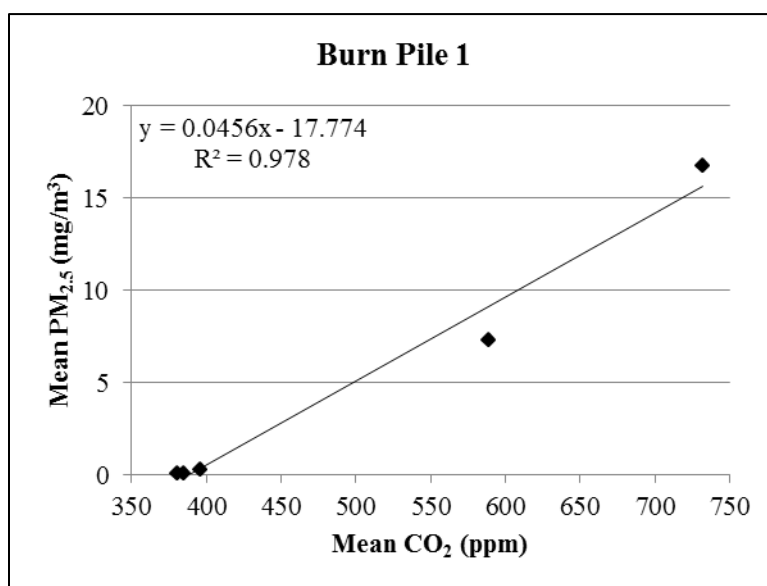
Figure 14: Linear fit of mean CO_2 and $PM_{2.5}$ (Burn Pile 1).

Figure 15: Linear fit of mean CO_2 and $PM_{2.5}$ (Burn Pile 2).

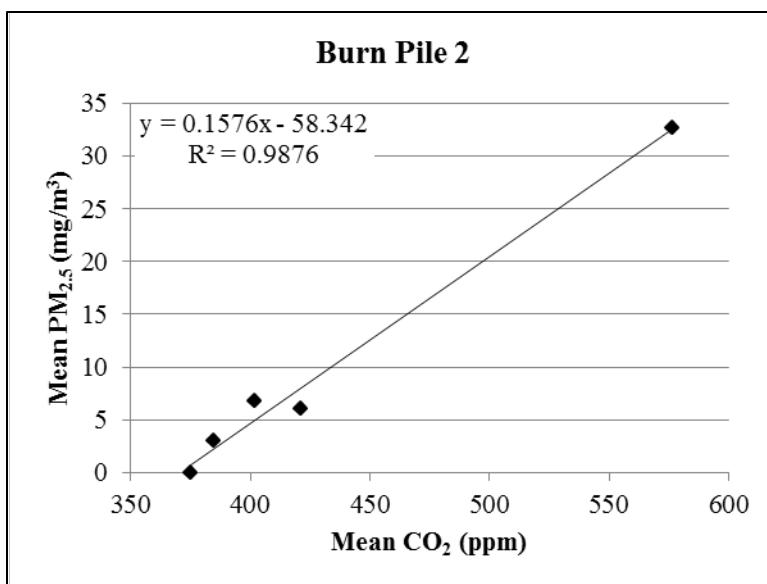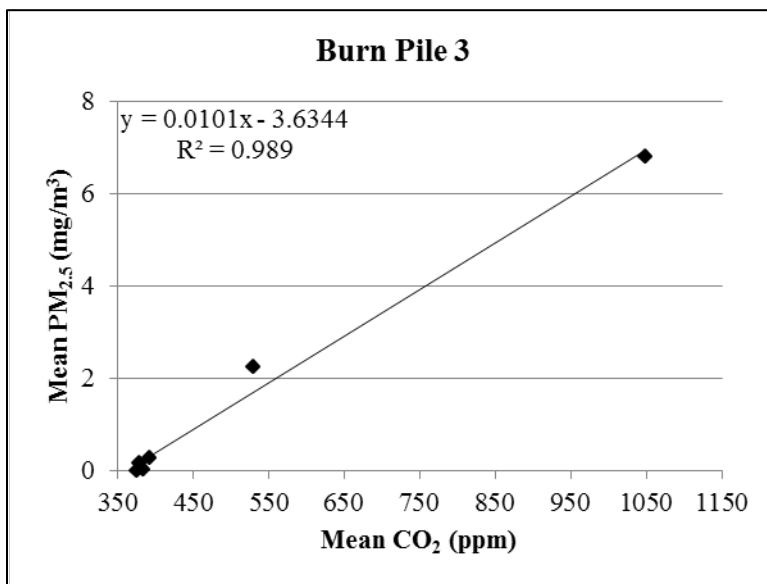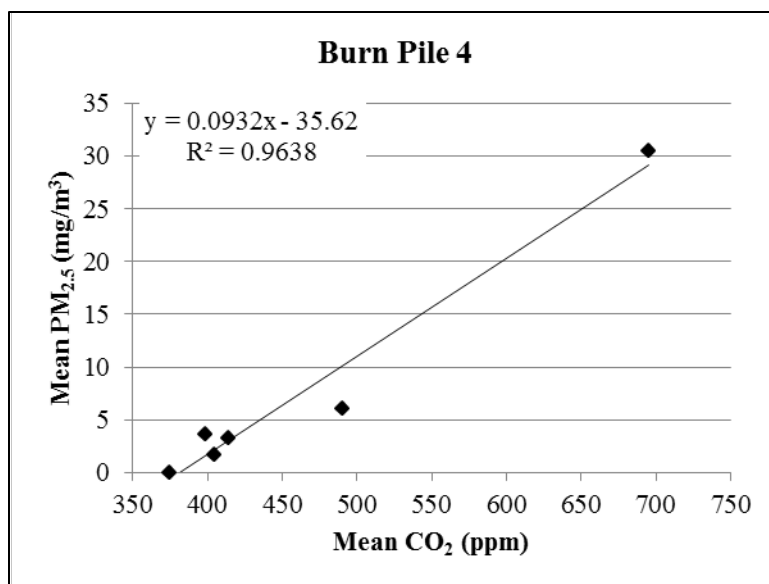Figure 16: Linear fit of mean CO_2 and $PM_{2.5}$ (Burn Pile 3).

Figure 17: Linear fit of mean CO_2 and $PM_{2.5}$ (Burn Pile 4).

References

The references used in this article are provided in the Bibliography section of the thesis, reformatted from that required by *Environmental Health Perspectives* to match the format adopted by this thesis.

III. Conclusions

Chapter Overview

      This chapter concludes the thesis in its entirety, to include a review of the findings of Chapter II as well as conclusions drawn from the expanded literature review and expanded results and discussions presented in Appendices A and B, respectively.   The following is a discussion on significance of the findings and the implications for potential future applications. Future research considerations will be discussed to conclude this chapter.

Review of Findings

The scope of this thesis was based upon the following questions:

1. Can surrogate analytes be used to estimate exposures to other POCs which may be too resource-intensive to otherwise sample on a routine basis?

    1.1. What POCs can be estimated using a surrogate analyte?

2. What is a potential assessment strategy for a risk assessor to estimate exposures throughout the installation?

Thesis Question 1: Surrogate Analyte Method.

      The use of CO_2 as a surrogate analyte to model $PM_{2.5}$ exposures was found to be a feasible tool. CO_2 sensors may provide a cost-effective solution for exposure monitoring, in lieu of air sampling methods requiring special collection kits and laboratory analysis or dependence on expensive PM DRIs. The surrogate model developed from this study requires mean surrogate analyte and POC measurements from background and the plume source. Interpolation between both endpoints could estimate exposures to the POC using the mean surrogate measurement at a given location.

Although similar findings have been used to estimate wildfire exposures, this conclusion is novel in that solid waste combustion emissions may be expected to vary greatly due to complex waste composition and burn parameters (EPA, 1997; Gullett and Raghunathan, 1997; Gullett et al., 2001; Lemieux et al., 2000; Olorunfemi et al., 2011; Reinhardt and Ottmar, 2004).

Thesis Question 1.1: Pollutants of Concern.

$PM_{2.5}$ was the POC analyzed for this research due to increasing implications of adverse health effects (Polichetti et al., 2009; Pope et al., 2002). Other pollutants that perhaps warrant exposure assessments include PCDD/Fs, polybrominated dibenzo-p-dioxins (PBDDs), polybrominated dibenzofurans (PBDFs), PAHs, PCBs, and VOCs. However, specific etiological POCs from waste combustion have not been conclusively identified, complicating the selection of future surrogate-POC pair studies (Abraham et al., 2012; IOM, 2011; Powell et al., 2012; Rose et al., 2012; Smith et al., 2012). Literature on exposure analysis of firefighter exposures to wild fires indicates potential correlations among these pollutants and other emissions. Coupled with the findings respective to Thesis Question 1, it is possible the surrogate model may be expanded to include other pollutants emitted from solid waste combustion.

Where sampling equipment is limited, or to augment an exposure assessment campaign with limited sampling equipment, a surrogate model may be implemented. This research only addresses the surrogate-POC pair of CO_2 and $PM_{2.5}$. As suggested in the literature, future research on solid waste combustion surrogate-POC pairs may yield other useful models. A preferred surrogate is likely one that has affordable and reliable sensor technology, with a strong correlation with the POC.

Thesis Question 2: Potential Assessment Strategy.

An assessment strategy may vary depending upon the available resources. Deployable sampling kits are readily available, but require reach-back support for laboratory analysis and equipment procurement. Other items to consider include the manpower and number of samples required (to sample spatially-based populations-at-risk (PARs) and to achieve the desired statistical significance). The procedures for defining PARs at an installation, and assigning personnel to them, are detailed in technical guidance. Yet implementation, to include Defense Occupational and Environmental Health Readiness System (DOEHRS) entry, is still being refined (USAFSAM, 2013). In general, a health risk assessor should review the PARs and develop a waste combustion exposure assessment plan which will elucidate differences in exposures for different PARs.

A proposed strategy to document waste combustion exposure assessments conducted using a surrogate model in DOEHRS Environmental Health module (DOEHRS-EH) was presented (Appendix C). Data uploaded into DOEHRS-EH will be reviewed by US Army Public Health Command (USAPHC) for inclusion in longitudinal exposure records (LERs) (Schneider, 2013). A standardized approach for documenting estimated waste combustion exposures may reduce overall uncertainty of the developed exposure profiles, resulting in more accurate LERs.

Limitations

This research observed data collected during solid waste combustion. No other significant sources of CO_2 or $PM_{2.5}$ were present in the area. In a deployed setting, there

may be other sources contributing to exposures of combustion products. Examples of such sources include diesel generators, military vehicles, and aircraft. Determining relative contributions from solid waste combustion versus other point sources or naturally-occurring levels of pollutants is an important consideration.

In addition, this research only considered the emissions and exposures of pollutants from one solid waste combustion source. In a deployed environment, multiple burn pits or burn boxes may be working simultaneously, perhaps at different stages of combustion or different locations. Such operations may warrant further research and validation of the surrogate model.

Significance of Findings

As the cause-effect relationship between burn pit exposures and observed health effects remains unknown, burn pit exposure assessments will continue to be an important part of longitudinal exposure documentation. This research may lead to a viable estimation tool for the deployed health risk assessor under circumstances in which ideal sampling equipment is not available. Additionally, future applications may expand beyond the military; a surrogate model may assist environmental health risk assessments for local communities subjected to similar combustion emissions.

Future Research

   The following list summarizes possible issues to address in future research. There may be significant logistical or other practical matters that may challenge the pursuit of such topics and should be assessed by a prospective researcher.

- Repeat the methods of this research to address influence of other significant combustion sources, such as generators, vehicles, or local industry.

- Repeat the methods of this research to include other analytes, such as PCDD/Fs, PBDD/Fs, PCBs, PAHs, and VOCs. For such a study, inclusion of CO as a secondary surrogate analyte may be worthwhile.

- Repeat the methods of this research with more ground sample locations, to include multiple directions and distances with respect to the combustion source.

Appendix A. Expanded Literature Review

Appendix Overview

This expanded literature review provides additional background information illustrating the significance of the problem statement and objectives of this thesis. A summary of the toxicology and epidemiological studies constituting the current body of knowledge of exposures to burn pit emissions is included. Examples of sampling equipment are briefly reviewed to identify opportunities for DoD health risk assessors, should access and resources become available. Finally, sampling and analytical methods are listed to compare and contrast capabilities provided by the Environmental Protection Agency (EPA) methods and the sampling equipment demonstrated for potential DoD inclusion.

Toxicology

Health effects have been studied for several chemical groups: PCDD/Fs, PBDD/Fs, PAHs, PCBs, VOCs, and PM. In general, PCDDs, PCDFs, PAHs, and many PCBs exhibit similar health effects: carcinogenic, endocrine disrupting, mutagenic, and teratogenic effects. Combustion emits a complex mixture of these chemical compounds, which may lead to additive, synergistic, antagonistic, or potentiating interactions.

PCDDs and PCDFs.

PCDDs and PCDFs, often referred to in literature simply as dioxins and furans, respectively, are products of organic intermediates formed during non-ideal combustion mechanisms. General health effects of dioxins and furans include increased cancer risks, endocrine disruption, and *in utero* adverse health effects. Acute exposures may produce

chloracne and nonspecific gastrointestinal effects. The mechanisms of these toxic effects and the development of exposure guidelines for dioxins and furans are reviewed in several articles (Birnbaum and DeVito, 1995; Pedersen et al., 2010; Geusau et al., 2001).

PAHs and PCBs.

The specific toxicological mechanisms of a given PAH compound are dependent on the chemical structure. Generally, the health effects of PAHs include carcinogenic, endocrine disrupting, mutagenic, and teratogenic properties. A few PCBs are dioxin-like in structure and toxic mechanisms. Studies have shown that non-dioxin-like PCBs demonstrate antagonist and synergistic interactions with PCDDs and PCDFs. Reviews of toxicological studies of PAHs and PCBs are readily available (Arcaro et al., 1999; Tran et al.; Birnbaum, 1994).

VOCs.

VOCs emitted from incomplete combustion vary significantly in chemical structures; therefore, an attempt to generalize health effects and mechanisms is not practical. Two common VOCs of concern from incomplete combustion include benzene and styrene. Benzene, the basic aromatic structure found in PCDDs, PCDFs, and PAHs, targets bone marrow, leading to aplastic anemia, and results in chromosomal damage (Snyder et al., 1993). Styrene is highly lipid-soluble and is readily absorbed into the bloodstream from all exposure routes. Health effects of acute exposure include skin, eye, and respiratory tract irritation and depressed central nervous system (Leibman, 1975).

A health risk assessment conducted at Joint Base Balad, Iraq, detected two VOCs at elevated levels: acrolein and hexachlorobutadiene (Vietas et al., 2008). Inhalation of acrolein may cause eye, nose, and throat irritation, and decreased lung function (ATSDR,

2007). Inhalation of hexachlorobutadiene may cause nasal irritation. One human case study demonstrated hepatic effects, but results are inconclusive due to the presence of other solvents (ATSDR, 1994).

PM.

Fine particles are generated in combustion processes, with varying size distributions and chemical composition. A thorough review of the health effects of PM summarized that exposure to PM has been associated with myocardial infarction, atherosclerosis, heart rate variability, and pulmonary inflammation (Polichetti et al., 2009; Avakian et al., 2002). Further, ultrafine particles (smaller than 100 nm) have a larger capacity for adsorbing other combustion by-products, facilitating increased distribution through inhalation.

Epidemiology

In one study, asthma, constrictive bronchiolitis (CB), and acute eosinophilic pneumonia (AEP) were evaluated among deployed personnel (Rose et al., 2012). The odds ratio was 1.58 for deployed personnel developing asthma compared to non-deployed personnel. Analysis for CB showed 80 soldiers were referred to a major medical center; 38 patients were diagnosed with CB, of which 25 were never smokers. Among medical records for 183,000 military personnel who deployed to Iraq, 18 cases of AEP occurred, resulting in two deaths. All of the cases were smokers, with 78% of the cases recently beginning the habit. Out of this analysis, the study hypothesized that the early phases of smoking may cause changes to lung tissue, leaving it perhaps more susceptible to AEP mechanisms.

Another study focused on obstructive pulmonary disease (Abraham et al., 2012). Potential bias and errors were noted among the data reviewed. Obstructive pulmonary disease may have been preclinical during exams performed between deployments, erroneously linking disease with later exposures. Bias may have been introduced when doctors were aware of the patient's deployment status. Further complicating the research, smoking was suspected to account for the majority of cases, but the data did not link smoking status to individuals. Obstructive pulmonary disease was found to occur at a rate of 23.9 per 1,000 person-years for post-deployment populations, higher compared to the pre-deployment diagnosis rate of 19.0 per 1,000 person-years. Interestingly, total respiratory system symptoms were observed at a rate of 300.6 per 1,000 person-years for pre-deployment, higher than the post-deployment rate of 276.2 per 1,000 person-years.

The Millennium Cohort Study is currently in progress and solicits voluntary DoD personnel involvement. Follow-up data collection is performed every three years until 2022. Several studies assessing currently available data include observations on chronic bronchitis, emphysema, newly reported asthma, self-reported respiratory symptoms, and chronic multisymptom illness (CMI). Results based on the Millennium Cohort Study include the finding that exposures incurred within three miles of burn pits did not increase the risk of chronic bronchitis, emphysema, newly reported asthma, or self-reported respiratory symptoms, according to available data (Smith et al., 2012). CMI, characterized by symptoms of fatigue, mood or cognitive problems, and musculoskeletal discomfort, was not found to be associated with exposures to burn pits within a three mile radius (Powell et al., 2012).

Documentation of Exposure Assessments

DoD health risk assessors are responsible for documenting exposures for all individuals, with an overall goal of creating accurate LERs. The Air Force conducts occupational and environmental health site assessments (OEHSAs) and uses DOEHRS to document such exposures and follow up assessments (Department of the Air Force, 2010; Department of the Air Force, 2012). The information loaded into DOEHRS is used to produce a periodic occupational and environmental monitoring summary (POEMS), summarizing the measured risk assessments for an installation, as outlined by DoD instructions (DoD, 2008; DoD, 2011). The LER differs from the POEMS in that the LER is an established record for an individual, based upon his or her encountered exposures, while the POEMS is a general summary of exposures for a larger population (e.g., an installation) and is not linked to any individual.

One shortfall for accurate LER documentation relates to how PARs are established. A PAR is analogous to the industrial hygiene "similar exposure group" (SEG) concept as both terms are applicable to a group of personnel having similar exposures. The primary difference, however, is that a SEG is applicable to occupational exposures while a PAR is applicable to environmental exposures. The difficulty in establishing PARs is mainly due to the transient nature of personnel at an installation. The USAF has produced a technical guide to assist the OEHSA process, to include defining PARs, integrating SEG exposure profiles, and implementing DOEHRS (USAFSAM, 2013).

One effective method for documenting an environmental health exposure assessment based on modeling is to establish an Exposure Pathway for a location under

the Environmental Health module, then upload quantitative assessments under the "Samples-Air-Direct Reading" address in DOEHRS (Schneider, 2013). The framework of a proposed process is introduced in Appendix C.

Sampling Equipment

Air sampling allows health risk assessors to quantify pollutants and health hazards with defined accuracy and precision. The types of air sampling equipment and their corresponding analytical methods are dependent upon the analytes and laboratory availability and capabilities. Examples of air sampling kits, requiring laboratory analysis, and direct reading instruments applicable to combustion emission monitoring are summarized below:

Air Sample Collection and Analysis.

SKC Inc. (Eighty Four, PA) provides several air sampling products, two of which the USAPHC currently provide to and coordinate laboratory analysis for deployed health risk assessors: the Deployable Particulate Sampler (DPS) and Deployable Volatile Sampler (DVS) systems. In addition, SKC provides a Deployable Cartridge Sampler (DCS) system. Each kit is based around the SKC Leland Legacy air sampling pump, mounted inside a Pelican case assembly. Variations between the three kits include collection media, low-flow adapters, and calibrators. An example SKC DPS kit is shown in Figure 18.

Figure 18: Contents of the SKC DPS kit.

The SKC DCS kit differs from the SKC DPS kit by the media and sampling head that connects to the tubing. The assessor may select a polyurethane foam (PUF) cartridge for Method TO-9A analysis or an XAD-2 cartridge for Method TO-13A analysis, with both methods measuring PAHs, PCBs, pesticides, PCDDs, and PCDFs.

The SKC DVS kit includes sorbent tubes which are analyzed by Method TO-17 for a range of VOCs. The sampling train operates at a low flow rate, which is regulated by a valve on the sorbent tube holder, and requires a separate calibrator than the DPS and DCS sample trains. A field operational DVS kit is shown in Figure 19.

Figure 19: Operational SKC DVS kit.

The SKC DPS kit uses one of two impactor heads to selectively collect $PM_{2.5}$ or PM_{10}, as displayed in Figure 18. PM is quantified using gravimetric analysis, resulting in a time-weighted average concentration. USAPHC, or another analytical laboratory, can perform inductively coupled plasma (ICP) analysis to identify the metals collected on the filter. One limitation of the SKC DPS is the inability to monitor PM in real-time, potentially missing intermittent high concentrations of PM.

As an alternative to the SKC DPS system, Airmetrics™ manufactures the MiniVol Tactical Air Sampler (TAS). Despite the physical differences between the two companies' products, the MiniVol TAS collects $PM_{2.5}$, PM_{10}, or total suspended particles

(TSP) in a similar manner as the SKC DPS system, using impactor technology. A picture of an operational MiniVol TAS is provided in Figure 20.

Figure 20: MiniVol TAS (Airmetrics, 2012).

An alternative to the SKC DPS system and MiniVol TAS for quantifying PM is the use of traditional industrial hygiene air sampling pumps. NIOSH Methods 0500 and 0600 use gravimetric analysis to quantify total suspended particulate (TSP) and respirable dust (PM with a 4 µm median cut point), respectively. Both methods require the use of a personal air sampling pump, filter cassette, and in the case of Method 0600, a cyclone separator.

DRIs.

DRIs are often used in conjunction with, or in lieu of, sample collection methods which rely on further analytical techniques. DRIs provide faster results, but have limitations, possibly including lower accuracy and interferences from other analytes.

Two aerosol DRIs manufactured by TSI Inc. that may be useful to DoD health risk assessors are the AeroTrak® 9303 and the DustTrak™ DRX. Both measure PM with

aerodynamic diameters larger than 0.3 µm, and simultaneously measure the concentration

of three or more PM sizes. In addition, the DustTrak is capable of collecting PM on a

filter paper for laboratory analysis, such as ICP techniques, to identify the PM

compounds.

As discussed previously, surrogate analytes may present an assessor with simple

linear models to estimate other pollutant concentrations. CO_2 was used in this study, and

CO has been used to estimate occupational exposures in studies of wildfire firefighters

(Olorunfemi et al., 2011; Reinhardt and Ottmar, 2004). CO and CO_2 sensors are

produced by many manufacturers and are assembled within many types of monitors, such

as multi-gas meters used for indoor air quality or confined space work.

Sampling and Analytical Methods

Many of the samples collected by using equipment listed in the previous

subsection can be analyzed by methods equivalent or similar to those employed by the

EPA for the TEAD project. Table 5 provides a brief comparison between the Tooele

sampling equipment and the deployable kits, with respect to their applicable analytical

methods.

Table 5: Analytical methods for thesis data collection and deployable kits.

Target Analytes	TEAD Project		Deployable Sample Kits for Environmental/Area Sampling	
	Equipment/ Sample Media	Analytical Method	Equipment/ Sample Media	Analytical Method
PCDD/Fs, PBDD/Fs	PUF media	TO-9A	SKC DCS System w/ PUF cartridge	TO-9A
PAHs	XAD-2 sorbent media	TO-13A	SKC DCS System w/ XAD-2 cartridge	TO-13A
VOCs	6 L Summa Canister	TO-15	SKC DVS System	TO-17
Metals	Filter Paper	IO-3.4	SKC DPS System; Airmetrics MiniVol; TSI DustTrak DRX	User Option
PM	Filter Paper	Gravimetric	SKC DPS System; Airmetrics MiniVol; IH Sample Trains	Gravimetric; NIOSH 0500 & 0600

As illustrated by Table 5, PCDD/Fs, PBDD/Fs, and PAHs can be assessed using the same EPA Methods in a deployed environment as those used during the Tooele Project. Sampling media designed for personal air samples (i.e., mounting on lapels for breathing zone sampling) are also available.

The main difference between Methods TO-15 and TO-17 for VOCs is the use of different collection media and the respective extraction for analysis; both methods employ gas chromatography/mass spectrometry. The analytes quantified are largely similar between the two methods.

Method IO 3.4 uses inductively coupled plasma techniques to identify and measure metal compounds from a filter paper. An assessor may opt for this method, or choose another, such as NIOSH Method 7300.

Appendix B. Expanded Results and Discussion

Appendix Overview

This appendix supplements the Results and Discussion sections in Chapter II. The material presented in this appendix was deemed excessive for a prospective article for publication, but may provide additional insight to the inquiring academic.

Burn Pile and Burn Box Emission Analysis

Figures 21 – 24 display the crane sample ANOVA results, comparing the emission concentrations between each burn test. In summary, Burn Box 1 resulted in lower $PM_{2.5}$ concentrations than all other burn tests. Multiple additions of waste may have increased combustion efficiency, leading to lower emissions of pollutants, compared to the burn piles which were visibly observed to transition to smoldering stages. Burn Box 2, implementing the single-charge method, resulted in higher $PM_{2.5}$ concentrations than all other burn tests. Analysis considering Burn Box 1 being comprised of four sub-tests did not produce notable differences in conclusions. Note: the y-axis has been truncated to improve visual identification of the ANOVA diamonds in Figures 21 – 24; the original figures show numerous large outliers, effectively making the ANOVA diamonds indecipherable.
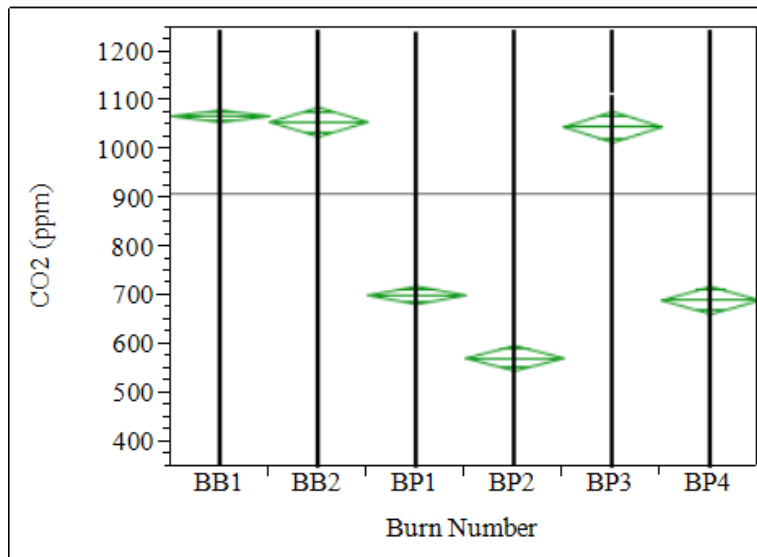
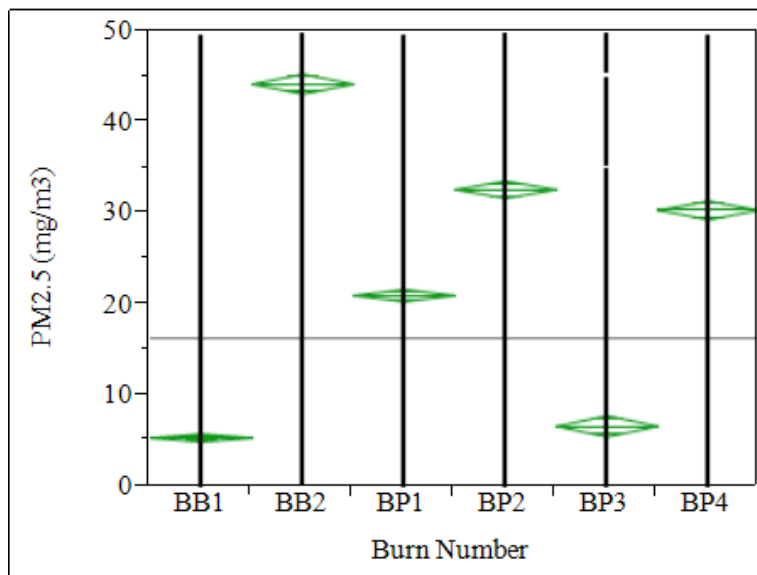Figure 21: CO_2 ANOVA considering Burn Box 1 as a single sample.

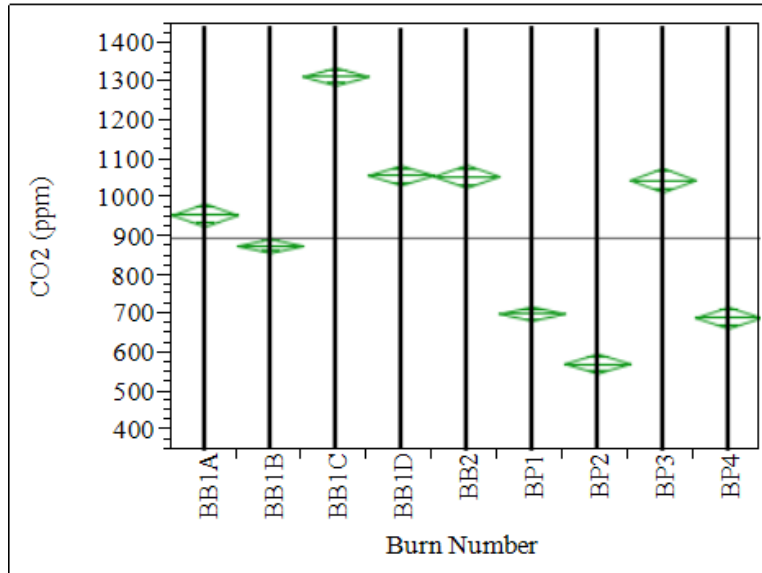Figure 22: $PM_{2.5}$ ANOVA considering Burn Box 1 as a single sample.

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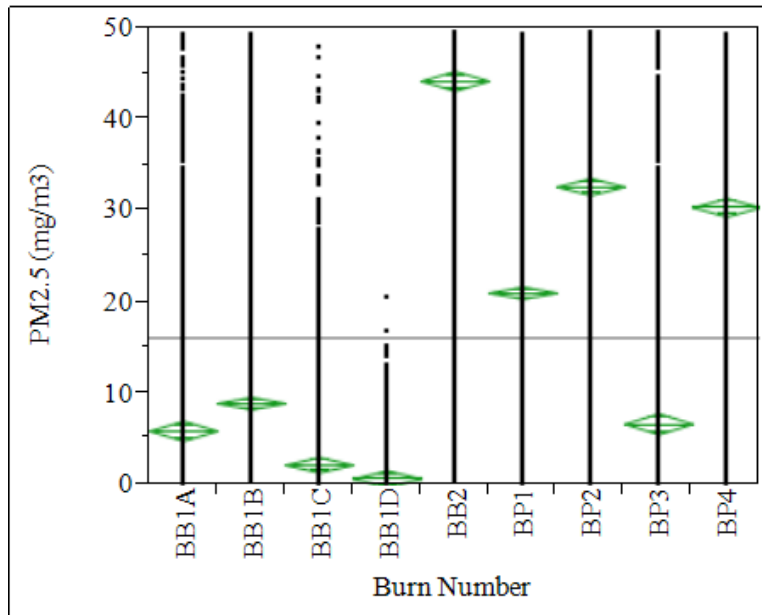Figure 23: CO_2 ANOVA considering Burn Box 1 as four sub-tests.

Figure 24: $PM_{2.5}$ ANOVA considering Burn Box 1 as four sub-tests.

Surrogate Model Analysis

While linear-fit plots were presented in Chapter II for the surrogate model, a general linear relationship describing each burn test was inferred using background and emission values as lower and upper bounds, respectively:

$$\hat{y} = y_i + \left(\frac{y_f - y_i}{x_f - x_i} \right)(x - x_i) \qquad (1)$$

where $\hat{y}$ is the predicted mean $PM_{2.5}$ (mg/m³), y_i is the background mean $PM_{2.5}$ (mg/m³), y_f is the emission mean $PM_{2.5}$ (mg/m³), x_f is the emission mean CO_2 (ppm), x_i is the background mean CO_2 (ppm), and x is the measured mean CO_2 at a sampling platform.

To illustrate the surrogate model and its application, the background mean CO_2 (x_i) and $PM_{2.5}$ (y_i) at TEAD were 375 ppm and 0.004 mg/m³, respectively. For Burn Pile 2, the base of the plume produced mean CO_2 (x_f) and $PM_{2.5}$ (y_f) emissions of 577 ppm and 32.712 mg/m³, respectively, as measured by the Flyer mounted on the crane. The mean CO_2 (x) measured at a ground station (40 m) was 421 ppm. Using Equation 1 yields a mean $PM_{2.5}$ concentration at the ground station as 7.452 mg/m³, compared to the measured mean $PM_{2.5}$ of 5.998 mg/m³, a 24.2% overestimation.

The surrogate model described by Equation 1 was developed independent of any distance component. The purpose of this is due to many unrelated variables that cannot be simplified for generic use. For example, wind speed and direction can be complex parameters, complicating exposure estimations. Another justification for the format of

Equation 1 is that emission compounds are assumed to disperse uniformly and homogenously throughout the region. Indeed, such an assumption is inherent within plume modeling programs, as studied by Oppenheimer (2012). CO_2 and $PM_{2.5}$ are assumed to be emitted from the source and disperse throughout the region uniformly; spatially, the decrease in the mean concentration of one compound was assumed to be analogous to the other compound, approaching background values at some distance.

The range of mean $PM_{2.5}$, as measured from real-time data at ground stations, was $0.019 - 44.369$ mg/m^3 ($19 - 44,369$ µg/m^3). The 24-hour and 1-year "Negligible" military exposure guidelines (MEGs) for $PM_{2.5}$ are 65 µg/m^3 and 15 µg/m^3, respectively (Department of the Army, 2010). The burn tests only lasted approximately three hours and a direct comparison to the MEGs cannot be made. However, it may be inferred that should these concentrations be sustained, short-term and long-term DoD limits would be exceeded under certain circumstances.

Appendix C. Draft Assessment Strategy

Appendix Overview

This appendix is a draft format of a potential future technical guide or procedure for a deployed health risk assessor. The air sampling products listed here are only examples; other viable sampling kits from other manufacturers may be similarly appropriate. This thesis did not compare operational capabilities between any products.

The following procedures assume a robust implementation of OEHSA principles and DOEHRS as required by the USAF (DoD, 2008; DoD, 2011; Department of the Air Force, 2010; Department of the Air Force, 2012). Other services may vary in their implementation of DOEHRS.

Exposure Assessment

Locations chosen for exposure assessment should be selected based off of well-established PARs and the exposure monitoring program.

Ideal Scenario.

The following analytes can be directly quantified with the equipment and supplies listed below. Several of these items were used for the research.

- PCDD/Fs, PBDD/Fs, PAHs, and PCBs: Air sampling kits, such as the SKC DCS System, can be used to quantify numerous compounds belonging to these chemical groups.

- VOCs: Air sampling kits, such as the SKC DVS System, can be used to quantify numerous VOCs.

- Metals: Filter paper collected from samplers such as Airmetrics MiniVol, SKC DPS System, or TSI DustTrak DRX may be analyzed by an analytical method using ICP.

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- PM$_{2.5}$ (and other sized PM): Sample collection methods, such as the use of Airmetrics MiniVol or SKC DPS System, require gravimetric analysis. The interchangeable components of the SKC kits, in addition to allowing metal analysis, suggest that the DPS kits would be useful to deployed assessors. Alternatively, DRIs may be more appropriate, as results are real-time and gravimetric analysis results may not be attainable in an austere environment.

Implementing the Surrogate Model.

To implement the surrogate model technique, it is assumed that background data have been adequately obtained for the surrogate analyte and the pollutant of concern to be estimated. Further, the surrogate model requires sampling for the surrogate analyte and the pollutant of concern at the source of solid waste combustion.

1. Identify the background (ambient) surrogate analyte concentration (x_i) and POC concentration (y_i).

2. Establish monitoring capabilities at the source of solid waste combustion, maintaining the monitoring equipment in the plume and near the source as close as feasible without damaging the equipment.

    2.1. Upon completion of exposure assessments, obtain the mean concentrations of the surrogate analyte (x_f) and POC (y_f).

3. Determine site(s) for exposure assessments. Set up a monitor for the surrogate analyte (e.g. CO$_2$ monitor) at the site. Record the mean (e.g. time-weighted average) value (x).

4. Calculate the estimated exposure for the POC ($\hat{y}$) using Equation 1:

$$\hat{y} = y_i + \left(\frac{y_f - y_i}{x_f - x_i} \right)(x - x_i)$$ **(1)**

Exposure Documentation

SEGs and PARs should be established in accordance with USAF guidance and at a granularity adequate for differentiating exposures between exposure groups (Department of the Air Force 2010; Department of the Air Force, 2012; USAFSAM, 2013). Multiple PARs are likely more appropriate rather than using a single PAR to represent the entire installation. For example, sleeping quarters may be one PAR at an installation, or multiple sleeping quarters may warrant multiple PARs, if exposures are reasonably different (e.g. sleeping quarters in the northwest lie downwind of a burn pit field, according to predominant wind data). Therefore, an individual may be assigned to several SEGs and PARs. Spatial and temporal differences are factors affecting exposures, including for waste combustion emission exposures.

Exposure pathways may be established in DOEHRS from an OEHSA (the procedure for accomplishing this will not be discussed here). Alternatively, exposure pathways can be established separate from the OEHSA and may be desirable under certain circumstances (i.e. a routine OEHSA update is not in progress, the pathway can be quantified in greater detail beyond that appropriate in the OEHSA, etc.).

A quantitative exposure assessment using a surrogate model for an exposure pathway can be performed in DOEHRS through the Environmental Health module, where inclusion into the LER is possible from further USAPHC operations. A standardized approach will ensure effective exposure documentation; specific steps for performing this task are proposed in the following section.

Exposure Pathways.

A DoD health risk assessor may elect to define an exposure pathway in

DOEHRS-EH separate from the OEHSA component. Guidance is available for this

procedure; this section is intended to supplement current guidance, proposing inputs

regarding waste combustion exposure assessments using a surrogate method. The

following section was based on the use of DOEHRS Demo using minimal simulated

location data.

Figure 25 is the display of DOEHRS where a user can define a new Exposure

Pathway by clicking the "+" icon.

Figure 25: DOEHRS-EH Exposure Pathway main screen.

The resulting detail page should be populated according to guidance and local professional judgment. Figure 26 demonstrates the type of information that may be appropriate for Exposure Pathways for modeled waste combustion exposure assessments.

Figure 26: Exposure Pathways details page with example information inputs.

Personnel can be assigned to Exposure Pathways (Figure 27). Exposures associated with personnel linked with an Exposure Pathway will be documented in their Exposure History Report, leading to their LERs (Schneider, 2013). There are logistical

concerns about large-scale maintenance in personnel assignments within DOEHRS. As

the demonstration presented here is limited to simulation, no personnel were assigned to

the location, and users should follow guidance to accomplish this.

Figure 27: Exposure Pathways details page displaying personnel assignment section.

Attachments may be uploaded in the Exposure Pathway component, as shown in

Figure 27, where the health risk assessor can provide additional information for review

by those responsible for developing individual LERs. The attachments should provide

details of the exposure assessments associated with the Exposure Pathway.   Figure 28 is

an example Word document providing details of the exposure assessment, to include the

implementation of a surrogate model. Note: The uncertainty factor shown in Figure 28

was arbitrarily established and is for demonstration only. Should an exposure assessment

be conducted implementing the surrogate model, the procedures for an uncertainty factor

should be developed in accordance with similar policies and procedures in addition to

further research.

DOEHRS-EH Exposure Pathway Attachment: Assessment

Exposure Pathway Name:		
Burn Pit exposures at Guard Tower		
Location/Base:	**Sampling Point:**	**Building:**
Base Camp 1 Test	Guard Tower	N/A
Coordinates:	39°49'23"N	084°02'58"W
Date:	**Sample Time:**	**Assessors Name:**
1 Mar 2013	0800 – 1600 Hr	Capt Michael Schmidt

Exposure Assessment Details and Conditions:

Sampling Equipment:	LI-COR® 820, s/n 12345					
Chemical:	CO_2 (used as a surrogate analyte to estimate $PM_{2.5}$ exposure)					
MEG:	24-hr "negligible": 0.065 mg/m^3 1-yr "negligible": 0.015 mg/m^3					
Source:	Burn Pit (~ 25 m from sample location)					
Duration of sampling:	8 hrs					
Duration of occupants' exposure:	6 – 8 hrs					
Number of occupants:	3					
Special Conditions or any additional ventilation:	Area monitored is elevated ~ 5 m from ground level; open to outdoors.					
Other potential sources:	Idle generators, generally downwind from sampling.					
Environmental Conditions:	Outside Temperature (°F):	88	Outside Relative Humidity (%):	76	Wind Information:	10 mph NNE
	Inside Temperature (°F):	N/A	Inside Relative Humidity (%):	N/A	Precipitation:	None

Figure 28: Example DOEHRS attachment describing the exposure assessment.

Surrogate Model Estimation:

Analyte	CO$_2$	PM$_{2.5}$
Sampling Equipment:	LI-COR® 820, s/n 67890	DustTrak™ 8520, s/n: 54321
Ambient background: (measured date/time)	375 ppm 28 Feb 2013 / 2300 hr (burn operations ceased for 8 hrs)	0.004 mg/m^3 28 Feb 2013 / 2300 hr (burn operations ceased for 8 hrs)
Burn Pit Plume (Average):	732 ppm	0.504 mg/m^3
Location measurement (TWA):	400 ppm	---

$$\hat{y} = y_i + \left(\frac{y_f - y_i}{x_f - x_i} \right)(x - x_i)$$

where $\hat{y}$ is the predicted mean PM$_{2.5}$ (mg/m^3), y_i is the background mean PM$_{2.5}$ (mg/m^3), y_f is the emission mean PM$_{2.5}$ (mg/m^3), x_f is the emission mean CO$_2$ (ppm), x_i is the background mean CO$_2$ (ppm), and x is the measured mean CO$_2$ at a sampling platform.

$$\hat{y} = 0.004 + \left(\frac{0.504 - 0.004}{732 - 375} \right)(400 - 375)$$

$$= 0.039$$

The estimated PM$_{2.5}$ exposure is 0.039 mg/m^3 (39 μg/m^3).

Uncertainty:

A 25% uncertainty factor is attributed to the surrogate model. For this exposure assessment, the uncertainty factor is:

$$= \pm 0.25 \cdot \left(0.039 \text{ mg/m}^3 \right)$$

$$= \pm 0.010 \text{ mg/m}^3$$

Notes:
The burn pit was in progress from approximately 0730 – 1630 hr. The wind direction was dominantly in the NNE direction at 10 mph, but the plume visibly shifted closer to the guard tower between 1100 and 1300 hr.

Surrogate Model Reference:

Schmidt, Michael A. *Health Risk Assessments of Waste Combustion Emissions Using Surrogate Analyte Models*. MS thesis, AFIT-ENV-13-M-26. School of Engineering and Management, Air Force Institute of Technology (AU), Wright-Patterson AFB OH, March 2013.

Figure 28 (continued): Example DOEHRS attachment describing the exposure assessment.

Multiple attachments using the template presented in Figure 28 may be appropriate, one for each exposure assessment. Another attachment summarizing all exposure assessments may assist the process in which the exposures are incorporated into the individuals' LERs. An example of a single document, updated with each exposure assessment, is provided in Figure 29.

DOEHRS-EH Exposure Pathway Attachment: Assessment History

Exposure Pathway Name:		
Burn Pit exposures at Guard Tower		
Location/Base:	**Sampling Point:**	**Building:**
Base Camp 1 Test	Guard Tower	N/A
Coordinates:	39°49'23"N	084°02'58"W

Summary of $PM_{2.5}$ exposures estimated via CO_2 measurements using a surrogate model. See individual assessment attachments in the Exposure Pathway in DOEHRS.

Assessment Date	Mean CO_2 (ppm) (at Sampling Point)	Estimated Mean $PM_{2.5}$ (mg/m^3)	Estimated Mean $PM_{2.5}$ Range (25% uncertainty factor)
1 Mar 2013	400	0.039	0.029 – 0.049
8 Mar 2013	529	0.260	0.325 – 0.325

Figure 29: Example DOEHRS attachment summarizing exposure assessments.

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14. ABSTRACT

Exposure assessments of open burn pits are often complicated by a lack of sampling equipment and resources. This research investigated the hypothesis of carbon dioxide (CO_2) as a viable surrogate for particulate matter with diameter ≤ 2.5 µm ($PM2.5$). Large-scale solid waste combustion tests resulted in linear trends between mean $PM2.5$ and CO_2 ($R^2 = 0.964 - 0.989$). This pilot study demonstrates the feasibility of using CO_2 as a surrogate of $PM2.5$ concentration as CO_2 sensors potentially provide a cost-effective solution for monitoring in lieu of expensive PM instruments. It also indicates the potential reduction in particulate matter when using batch-feeding practices with burn boxes (versus open burning).

15. SUBJECT TERMS
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